Electronic Supplementary Information:

Soft glassy colloidal array in ionic liquid, which exhibits homogeneous, nonbrilliant, and angle-independent structural colours

Kazuhide Ueno, Aya Inaba, Yuta Sano, Masashi Kondoh, and Masayoshi Watanabe*

Department of Chemistry and Biotechnology and Instrumental Analysis Center, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Materials.

The IL used in this study, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C_2mim][NTf_2]), was prepared by carrying out a metathesis reaction between freshly prepared [C_2mim]Br and Li[NTf_2], as described in our previous study.[1] The structure of the IL was identified by ^{1}H (400 MHz) and ^{19}F (376 MHz) NMR. Prior to use, the IL was dehydrated in high vacuum by heating it at 70 °C for 24 h. The water content of the IL was found to be 29 ppm, as determined by the Karl-Fischer titration (Mitsubishi Chemical Corporation, CA-07). The halides in the aqueous phases in contact with the IL could not be detected by using an $AgNO_3$ solution.

PMMA-grafted silica nanoparticles were synthesized by surface-initiated atom transfer radical polymerization (ATRP) from silica nanoparticles, by following the procedure reported in previous studies.[2–4] Monodisperse silica colloidal particles with diameters of 120 nm (KE-P10) and 220 nm (KE-W20) were obtained from Nippon Shokubai Co., Ltd. The PMMA grafts were cleaved from the silica cores by HF treatment. The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) were obtained by gel permeation chromatography (GPC). The graft density (ρ_g) of PMMA was calculated from the weight loss of the PMMA grafts, measured by thermogravimetric analysis (TGA) and the density of silica.[4] The average hydrodynamic radii (R_h) of PMMA-grafted silica particles were determined by conducting dynamic light scattering (DLS) measurement on the dilute suspensions of the PMMA-grafted particles in [C_2mim][NTf_2]. The obtained autocorrelation functions were analyzed by applying the third-order cumulant fitting.[4] The characterization results of PMMA-grafted silica particles are summarized in Table S1.

Table S1. PMMA-grafted silica particles used in this study

Sample	Silica core dia. (nm)	M_n	M_w/M_n	ρ_g (chains/nm^{-2})	R_h (nm)
Sample 1	120	91000	1.38	0.11	143
Sample 2	120	53000	1.28	0.21	107
Sample 3	220	67000	1.30	0.18	181

TEM observation of colloidal arrays in the IL.

The colloidal array was carefully applied on a collodion-coated TEM copper grid using a brush. A drop of THF was then poured on it to remove upper layers of the multilayered arrays and to leave the single array. Finally, the sample grid was dried. TEM observations were carried out using JEOL JEM-2000FXII operated at 100 kV.

Photographs, reflection and transmission spectroscopy.

Photographs of the samples were taken with a digital camera (Sony, Cyber-shot DSC-T50). Reflection spectroscopy was carried out by using an Ocean Optics USB2000 fiber-optic spectrometer equipped with a tungsten halogen lamp (Ocean Optics, LS-1) as the light source. Transmission spectra were recorded using a UV-Vis spectrophotometer (Shimadzu, UV-2500PC). The colloidal arrays were placed between two glass slides separated by a silicone spacer (1 mm thick).

Figure S1 and Figure S2 show photographs and the reflection spectra for the colloidal arrays, respectively. The structural colours were tunable over the entire visible region by precisely adjusting the particle size of the silica core and the chain length of the grafted polymer.

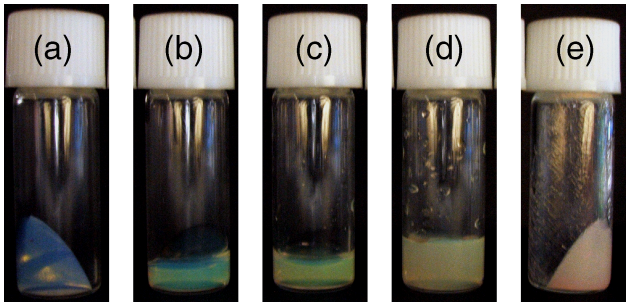

Figure S1. Photograph of soft glassy colloidal arrays in an IL: (a) 28.6, (b) 22.2, (c) 18.2, (d) 14.3 wt% for sample 1; (e) 50.0 wt% for sample 3.

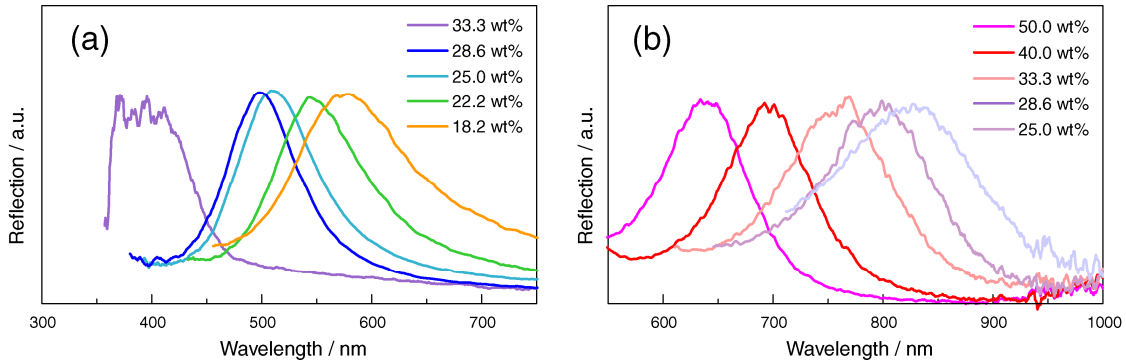

Figure S2. Reflection spectra of the colloidal arrays; (a) sample 2 and (b) sample 3.

Two-dimensional Fourier analysis.

The two-dimensional (2D) Fourier power spectra of the TEM images were obtained and the reflection spectra were predicted by following the procedure reported by Prum et al.[5] The digital TEM micrographs were analyzed using the matrix algebra program MATLAB R2007b (MathWorks). The Fourier transforms of the digital TEM images were calculated by the 2D fast-Fourier transform algorithm. A portion of the colloidal array corresponding to an area of 1024 × 1024 pixel of the micrograph was selected for analysis. The spatial frequency expressed in pixel^{-1} obtained in the power spectra was converted into spatial frequency expressed in nm^{-1}, with a scale factor of nm pixel^{-1}. The scale factor of each image was calculated from the number of pixels in the scale bar of the TEM image.

Reflection spectra were predicted from the radial averages of the 2D Fourier power spectra and mean refractive indices of the colloidal arrays in the IL. A radial average of the total percentage power was calculated for concentric bins of the ring-shaped power spectrum corresponding to hundred 10-nm-wide wavelength intervals between 300 and 800 nm. The radial average of total percentage power was expressed in terms of percentage of visible Fourier power by normalizing the total percentage power across the visible spatial frequency (i.e., in range of 300–800 nm). Finally, the inverse of each of the special frequency averages for each wavelength was multiplied by 2 and by the average refractive index of the system, and then expressed in terms of wavelength (nm). The average refractive indices were calculated from a two-partition histogram of the image darkness. The refractive index of silica core was taken as 1.46 (the darker portion in the TEM image). The refractive index (n_{light}) of the lighter portion that corresponds to PMMA and the IL was calculated from the following equation.

$$n_{\mathrm{light}}{}^2 = n_{\mathrm{IL}}{}^2\phi_{\mathrm{IL}} + n_{\mathrm{PMMA}}{}^2\phi_{\mathrm{PMMA}}$$
$$(\phi_{\mathrm{IL}} + \phi_{\mathrm{PMMA}} = 1)$$

where n is the refractive index, and ϕ is the volume fraction. In this study, we substituted the values of 1.43 and 1.49 for n_{IL} and n_{PMMA}, respectively. Because ϕ_{IL} and ϕ_{PMMA} depend on the concentration of the PMMA-grafted particles in the IL, the resulting n_{light} varied with concentration and was found to be in range of 1.431–1.424.

References

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